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COUPLING OF POLY(LACTIC ACID) WITH A POLYURETHANE ELASTOMER BY REACTIVE PROCESSING

Dániel Bedő[1,2], Balázs Imre[1,2*], Attila Domján[3], Peter Schön[4], G. Julius Vancso[4] and Béla Pukánszky[1,2]

[1]Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary

[2]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1525 Budapest, P. O. Box 17, Hungary

[3]Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1525 Budapest, P. O. Box 17, Hungary

[4]Materials Science and Technology of Polymers, MESA$^+$ Institute for Nanotechnology, University of Twente, Enschede, NL-7500, The Netherlands

*Corresponding author: Phone: +36-1-463-2967, Fax: +36-1-463-3474, E-mail: bimre@mail.bme.hu

ABSTRACT

A segmented polyurethane elastomer (PU) was synthesized in poly(lactic acid) (PLA) melt by reactive processing. The isocyanate component was expected to react with the end-groups of PLA resulting in the formation of block-copolymers. The stoichiometry of the functional groups, i.e. the isocyanate (NCO)-active hydrogen [H(a)] ratio, was optimized in the preliminary experiments. Mechanical properties changed drastically at small NCO/H(a) ratios and remained practically constant above 1.0. Two different processing methods were compared in the further experiments: conventional mixing of PU with PLA (PLA/PU), and reactive blending (PLA-b-PU). The comparison of the structure and properties of compatibilized reactive blends and conventional physical blends clearly showed the benefits of reactive processing. The coupling of the phases resulted in a finer dispersion of the particles in the matrix leading to better mechanical properties in the reactive blend. The successful synthesis of PLA-b-PU block copolymers was confirmed by NMR spectroscopy. The isocyanate component was found to react only with the hydroxyl end-groups of PLA, while the formation of amide and acylurea groups was not detected on the carboxyl end.

KEYWORDS: poly(lactic acid), segmented polyurethane elastomer, reactive compatibilization, chemical composition, structure and properties

1. INTRODUCTION

Biopolymers have large potential and several advantages. They are either biodegradable or can be produced from renewable resources, and most of them are biocompatible making them ideal candidates for biomedical applications. However, they possess some drawbacks as well. In spite of increasing production capacity, bio-based and biodegradable alternatives are still expensive compared to commodity polymers and their properties are also often inferior, or at least do not correspond to the expectations of plastics converters or users. The performance of biopolymers must be improved considerably to utilize their potentials and penetrate new markets. Consequently, the modification of these materials is in the focus of scientific research.

For various reasons both industrial and scientific interest increased in poly(lactic acid) (PLA) in recent years [1,2]. Hopes are rising that this material may present an alternative to commodity polymers in several fields of application. However, the rapid physical ageing of PLA results in a brittle material with low impact resistance [3], thus most studies aim to improve this property by either plasticization [4] or blending with various elastomers [5-9].

Polyurethanes (PU) represent a versatile group of polymeric materials applied in various areas from medicine [10,11] to construction and the automotive industry [12]. Although thermoplastic PU elastomers [13,14] possess excellent mechanical properties and their outstanding biocompatibility [16] allows their use in biomedicine, these polymers are surprisingly rarely considered for the impact modification of PLA. The few examples existing [17,18], however, are quite promising, reporting good compatibility of the components and considerable increase of toughness upon the introduction of a PU elastomer into poly(lactic acid).

Blends of poly(lactic acid) with segmented polyurethane elastomers can be obtained by simple physical blending, under which term we understand the mixing of polymeric materials in the melt state with no chemical reactions taking place. A wide range of properties can be achieved by this approach to meet the requirements of targeted applications in relatively short time and for low cost compared to the development of new monomers and polymerization techniques.

However, very few polymer pairs are miscible or even compatible with each other, thus the characteristics of the resulting blends are generally unsatisfactory. Compatibilization is needed to achieve properties required for specific applications [19]. Compatibilizers are either small or large molecular weight compounds showing interfacial activity in heterogeneous polymer blends [20]. The compatibilizing effect is usually attributed to an increase in interfacial adhesion and to the formation of smaller dispersed particles resulting in improved mechanical properties. Different strategies of compatibilization can be distinguished. In the case of nonreactive methods, premade amphiphilic compounds, e.g. block copolymers, are added to the blend, one constitutive end or block being miscible with one blend component, while the other with the second [21,22].

Unfortunately, physical compatibilization has its limitations. The characteristics of materials can be adjusted in a much wider range by reactive compatibilization, thus improving the application possibilities of polymer blends [23]. In this case the compatibilizer forms in situ during blending as a result of the addition of polymers with reactive groups [24-26] or small molecular weight chemicals [24,27,28]. The synthesis of one polymer in the presence of another might also result in blends containing grafted or block-copolymers acting as compatibilizer. This latter approach can be implemented for biopolymers, like poly(lactic acid) or starch, as reported by Dubois et al. [29,30]. The ring-opening polymerization (ROP) of cyclic esters initiated by the hydroxyl groups of biopolymers like starch [29], dextran [30] or partially substituted cellulose acetate (CA) [31,32] is a convenient method for the preparation of block copolymers by reactive processing. Numerous other combinations are also possible [33,34].

Although many studies describe solvent based, laboratory scale techniques [35], the true potential of reactive compatibilization lies in reactive processing in melt. Apart from the environmental benefits of a solvent-free process, these methods are generally less time-consuming and also cheaper, since conventional processing equipment can be used for one-step blending and compatibilization with all the advantages of a chemical approach [36]. The considerable potential of this method consists in the fact that structure and properties can be controlled relatively easily by the proper selection of agents, blend composition and processing conditions.

The synthesis of a segmented polyurethane elastomer in poly(lactic acid) melt is reported in our present communication. In an earlier paper [18] we compared the morphology and properties of blends prepared by conventional mixing of PU with PLA (PLA/PU) and by reactive blending, i.e. the polymerization of polyurethane in PLA melt (PLA-b-PU). In this latter case the isocyanate component is expected to react with the end-groups of PLA resulting in the formation of block-copolymers. Here we aim to confirm our hypothesis, focusing on the chemical background of the process, besides demonstrating the feasibility of reactive compatibilization of this specific blend by the coupling of the phases.

2. EXPERIMENTAL

2.1 Materials, sample preparation

The poly(lactic acid) used in the experiments was obtained from NatureWorks (USA). The selected grade (Ingeo 4032D, M_n = 88 500 g/mol and M_w/M_n = 1.8) is recommended for extrusion. The polymer (<2 % D isomer) has a density of 1.24 g/cm^3, while its MFI is 3.9 g/10 min at 190 °C and 2.16 kg load. Polytetrahydrofuran (PTHF, M_n = 1000 g/mol), 1,4-butanediol (BD) and 4,4′-methylenebis(phenyl isocyanate) (MDI) for polyurethane synthesis were obtained from Sigma-Aldrich. Both poly(lactic acid) and PTHF were dried in a vacuum oven before further use (110 °C for 4 hours and 80 °C for 4 hours, respectively). 1,4-butanediol was vacuum-distilled in order to remove any traces of water, while MDI was used as received.

In the case of consecutive polymerization and blending, both polyurethane synthesis (150 °C, 50 rpm, 30 min) and the homogenization of PLA and PU (180 °C, 50 rpm, 12 min) were carried out in an internal mixer (Brabender W 50 EHT). The same equipment was used for the one-step method, i.e. reactive processing (180 °C, 50 rpm, 20 min). Poly(lactic acid) was fed into the chamber first, followed by the addition of the diols (PTHF and BD) to the PLA melt, and the isocyanate (MDI) was added last. Both temperature and torque were recorded during homogenization. The melt was transferred to a Fontijne SRA 100 compression molding machine (190 °C, 5 min) to produce 1 mm thick plates used for further testing. Samples for the optimization of stoichiometry, i.e. the ratio of isocyanate (NCO) and active hydrogen containing groups [H(a)], were produced according to the one-step method with a polyurethane content of 30 vol%.

2.2 Characterization

In order to characterize their structure, PLA was selectively dissolved from the blends by extraction in dichloromethane. A 2 g sample was extracted with 160 ml solvent for 48 hours in a Soxhlet extractor. The extracted samples were dried in vacuum for 24 hours. The chemical structure and composition of the separated PLA and PU fractions were determined by solution state nuclear magnetic resonance spectroscopy (NMR). NMR spectra were obtained by using a Varian Unity INOVA spectrometer operating at the ^{1}H frequency of 600 MHz with 5 mm inverse detection probe, while a Varian Unity INOVA spectrometer operating at the ^{1}H frequency of 400 MHz with a Z-gradient 5 mm inverse detection probe was used for ^{1}H diffusion-ordered spectroscopy (DOSY). The ^{1}H-DOSY experiments were carried out using a Performa I gradient amplifier with a 20 Gauss/cm maximum gradient capability. The bipolar pulse-pair stimulated-echo (Dbppste) pulse sequence was used for acquiring diffusion data with 20 msec diffusion delay, 25 squared increments for gradient levels and 32 transients with a delay time of 16 sec. The Varian DOSY package was used for data processing. The sample was dissolved in deuterated chloroform (17 mg sample in 0.6 ml solvent). The signals of the solvent (7.26 ppm on the ^{1}H and 77.4

ppm on the ^{13}C scale) were used as reference for the chemical shifts. 16 sec delay time and 4 sec acquisition time were used to get accurate integrals from the one-dimensional ^{1}H spectra. Two-dimensional $^{1}H-^{13}C$ correlation spectra were recorded for assignation and to map the connections in a molecule. Homonuclear single-quantum correlation (HSQC) and heteronuclear multiple-quantum correlation (HMQC) measurements were carried out under standard conditions with 2 sec delay time to identify directly bonded C–H pairs and longer connections (2-3 bonds), respectively. The measurements were carried out at 25 °C.

Molecular weight was determined by size-exclusion chromatography (SEC). Chromatograms were recorded in dimethylformamide (DMF) at a flow rate of 0.5 ml/min at 35 °C with a Waters chromatograph (Waters e2695 Separation Module) equipped with four gel columns (4.6 * 300 mm, 5 µm Styragel columns: HR 0.5, 1, 2 and 4) and a Waters 2414 refractive index detector. Polystyrene samples of narrow molecular weight were used for calibration. The chromatograms were evaluated using the Empower 2 (Waters 2008) software.

The morphology of the blends was studied by microscopy. Scanning electron micrographs (SEM, JEOL JSM-6380 LA) were taken from cryo-fractured surfaces. Atomic force micrographs were recorded on smooth, cryomicrotomed cross-sections of selected samples. A Multimode 8 AFM instrument equipped with a NanoScope V controller and NanoScope version 8.10 software (Bruker Nano Surface) was used for the AFM measurements. Image processing and data analysis were performed with the NanoScope software version 8.10, and NanoScope Analysis software version 1.40. Tapping mode imaging and Peak Force Tapping was done with Si cantilevers (RTESPA, Bruker AFM probes) in air. Cantilever spring constants were determined using the thermal tune method and showed values in the range of ~20–40 N/m. For DMT modulus measurements the cantilevers were calibrated using a standard PS sample. PeakForce Quantitative Nanomechanical Property Mapping (PF-QNM) AFM was done at a constant oscillation of the sample at 2 kHz using amplitudes of 150 nm. Scanning was performed at a speed of 1–2 lines/s.

Mechanical properties were characterized by tensile testing on standard ISO 527 5A specimens with a thickness of 1 mm using an Instron 5566 apparatus. Stiffness (E) was determined at 0.5 mm/min cross-head speed and 50 mm gauge length. Tensile strength (σ) and elongation-at-break (ε) were calculated from force vs. deformation traces measured on the same specimens at 5 mm/min cross-head speed.

3. RESULTS AND DISCUSSION

3.1 Optimization of stoichiometry

MDI and butanediol form the hard segments, while the soft segments are blocks containing mostly PTHF units in the polyurethane synthesized in our study. The stoichiometric ratio of the functional groups has to be optimized in order to obtain high molecular weight polymer in the reaction. Slight isocyanate excess is usually applied because of the inevitable presence of some traces of water and other impurities [38].

When conducting the polymerization in PLA melt, the isocyanate group is expected to react with both the hydroxyl and carboxyl end-groups of poly(lactic acid) leading to the formation of PLA-b-PU block copolymers acting as compatibilizer (**Fig. 1**). Although reactions with the carboxyl groups might result in carbon dioxide formation, this should not lead to any difficulties in processing, because of the large molecular weight and thus the small number PLA end-groups. Indeed, foaming was not observed during the production of any of the samples. Nevertheless, the ratio of isocyanate and active hydrogen containing groups, i.e. NCO/H(a), where H(a) refers to the number of PTHF, BD and PLA end groups, had to be optimized, because of the possible side reactions and the presence of traces of water.

The torque measured during reactive processing is in direct correlation with the viscosity of the melt. Since that of PLA remains constant, or decreases slightly as a result of degradation, any increase in viscosity must be related to an increase in the molar mass of the forming polyurethane as shown in **Fig. 2.** We investigated the effect of the NCO/H(a) ratio in blends containing 0.3 volume fraction polyurethane. As expected, equilibrium viscosity of the melt increases as the ratio of isocyanate and active hydrogen containing groups approaches 1 (**Fig. 2a**), while smaller torque was recorded at larger NCO excess (**Fig. 2b**). In this latter case, however, melt viscosity increases continuously even at long processing times without reaching a plateau, most likely as a result of the formation of a cross-linked structure in the reaction of excess isocyanate with the urethane groups [15]. Cross-links in the polyurethane phase can be advantageous in terms of improving the impact resistance of PLA, as Yuan and Ruckenstein pointed out [17]. Nevertheless, in order to preserve the thermoplastic character of the blend, such side reactions should be kept to a certain level limiting the isocyanate amount which can be applied. The tendency is even more obvious if we take a look at the torque measured at the end of the reactive processing as a function NCO/H(a) ratio, as presented in **Fig. 3**. This can be considered a good indicator of the effect of stoichiometry on the average molar mass of the polymer blend. Torque reaches a maximum at an NCO/H(a) ratio of approximately 1.00-1.05, implying high viscosity and thus a high degree of polymerization. As we discussed earlier, the maximum being slightly over 1.00 indicates side reactions consuming NCO moieties, most likely due to the presence of water.

As the perspective aim of the reactive blending procedure is the impact modification of PLA, deformability of the blends is of large importance. This characteristic correlates strongly with the molecular weight of the polyurethane fraction. The results presented in **Fig. 4** indicate that an NCO/H(a) ratio of at least 0.97 is needed to obtain a PU of high molecular weight and large elongation-at-break. Nevertheless, these results seem to be in contradiction with the tendency presented in **Fig. 3**, as the deformability of the blends remains constant at higher NCO/H(a) ratios despite the presumed decrease of molar mass. This behavior can be explained by the formation of hard domains – consisting of MDI and BD units – acting as physical crosslinks in the blends at room temperature, increasing deformability without affecting melt viscosity. Based on the above results, a slight NCO excess, NCO/H(a) = 1.01 was chosen for further investigations. Using this stoichiometry, physical and reactive blends were produced in the entire composition range from 0 to 1 PU contents in 0.1 volume fraction steps, and their properties were compared.

3.2 Structure and properties

The structure and properties of the reactive blends (PLA-b-PU) were compared to those of samples with the same composition but prepared by physical blending (PLA/PU). The morphology of the blends was analyzed by SEM (**Fig. 5**) and AFM (**Fig. 6**). Both methods show the formation of a heterogeneous structure in all samples, while significant differences can also be observed between the physical and the reactive blend. In the case of PLA excess this polymer is likely to be the continuous phase, although this can hardly be decided at 0.5 volume fraction PU based on SEM micrographs only (**Fig. 5**). Considering the AFM images shown in **Fig. 6**, however, we might conclude that PU is the dispersed phase at this composition, and phase inversion should occur slightly above 50 vol% polyurethane content. In the case of the reactive blends, AFM images (**Fig. 6b**) indicate the possible formation of a co-continuous phase structure at the same composition. The PU phase contains small PLA inclusions implying the possible development of a structural formation at the submicron scale at large PU contents. The formation of such a structure is a sign of good interactions and might also influence properties considerably.

The mechanical behavior of the segmented polyurethane elastomer differs considerably from that of poly(lactic acid). The latter, being a glassy polymer with large modulus, yield stress and tensile strength, suffers brittle fracture without neck formation at small elongation during tensile test as presented in **Fig. 7**. PU, on the other hand, has typical rubber-like behavior with excellent deformability (~ 600%) and reasonable strength. The effect of modified structure and improved interfacial adhesion of the reactive blends can be observed clearly on properties measured at large deformations. The coupling of the phases results in considerably larger strength at somewhat larger elongations showing the benefits of reactive processing. A more detailed analysis of the effect of compatibilization by reactive processing on the structure and properties of PLA-PU blends can be found in our previous publication [18].

3.3 Chemical structure of PLA-b-PU copolymers

As mentioned earlier, the isocyanate component is expected to react with poly(lactic acid) end-groups, both –OH and –COOH, during the synthesis of polyurethanes in PLA melt forming PLA-b-PU copolymers, and thus leading to a better dispersion of the PU particles as well as increased tensile strength. In order to confirm our hypothesis, the PLA fraction was selectively dissolved from the reactive blends, and the composition and chemical structure of both fractions were analyzed using solution state NMR spectroscopy. Only the presence of polyurethane and traces of impurities were detected in the PU fraction. The selectively dissolved material, on the other hand, was found to contain a certain amount of PU besides PLA. The solution state ^{1}H NMR spectrum of the PLA rich fraction dissolved from the reactive blend containing 40 vol% polyurethane is shown in **Fig. 8**. Peaks were assigned on the bases of two-dimensional ^{1}H-^{13}C and ^{1}H-^{1}H correlation spectra. Besides the signals of PLA and PU, the presence of a small amount of solvent (chloroform, dichlorometane – DCM) can also be detected in the spectrum. The relatively broad signals appearing around 1 and 0 ppm belong to oligomeric impurities originating from the polymerization and purification processes. As their larger diffusion coefficient in the DOSY spectrum suggests (2.5 vs. 0.5-0.8 m^2/s in **Fig. 9**) their size is much smaller than that of both polymers, thus they cannot be attached to PU or PLA chains. Their amount is small, less than 2 %. The presence of the signal at 5.9 ppm proves that polyurethane forms at the hydroxyl end of PLA (**Fig. 1a**), but signals belonging to amide groups forming on the carboxyl end-group or the formation of acylurea could not be found in the spectra. However, we have to note that the peak assigned to the free –OH end groups of PLA at ~4.4 ppm in **Fig. 8** indicates the presence of unmodified poly(lactic acid) without PU units attached. From the integral values we can estimate that PU units are attached to approximately 40% of the PLA chains.

A DOSY experiment was carried out in order to prove the formation of PLA-b-PU block copolymers and to gain information on the size and size distribution of the polymeric components. As the dotted line in **Fig. 9** shows, the polyurethane component (signals 4-15) has nearly the same diffusion coefficient, i.e. 0.5-0.8 m^2/s, as the PLA molecules (signals 1 and 2 in the DOSY spectrum) suggesting that their molar mass is also similar. Data processing of the DOSY spectra focusing on overlapping signals assigned to molecules of different size has clarified the similarity of the diffusion coefficients. 10-20 % of the PU signals belong to oligomeric PU units, while the major component has the same diffusion coefficient, thus the same molar mass, as the PLA component. This is only possible if the signals belong to the same macromolecules, i.e. the polyurethane molecules are chemically bonded to the hydroxyl end-groups of poly(lactic acid). As mentioned above, unmodified PLA molecules and a small amount of oligomeric PU are also present besides the PLU-b-PU units in the blend obtained by reactive processing. The exact molecular size of the components cannot be determined because of the different solvation properties of the chemically dissimilar molecules of the two polymers.

4. CONCLUSIONS

Poly(lactic acid) was modified by blending with a segmented polyurethane elastomer. The phases were coupled chemically by the synthesis of the polyurethane in the PLA melt in order to improve structure and interfacial adhesion. The ratio of isocyanate and active hydrogen containing groups was optimized based on tensile testing and the evaluation of torque recorded during processing. The comparison of the structure and properties of compatibilized reactive and conventional physical blends, respectively, clearly shows the benefits of reactive processing. The coupling of the phases and the advantageous morphology of the reactive blends results in improved mechanical properties compared to the traditional physical blend. NMR measurements confirmed that the isocyanate component reacts with the hydroxyl end-groups of PLA during reactive processing, resulting in the formation of PLA-b-PU block copolymers. The formation of amide and acylurea groups on the carboxyl end of PLA was not detected in the reaction product.

5. ACKNOWLEDGEMENTS

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Figures

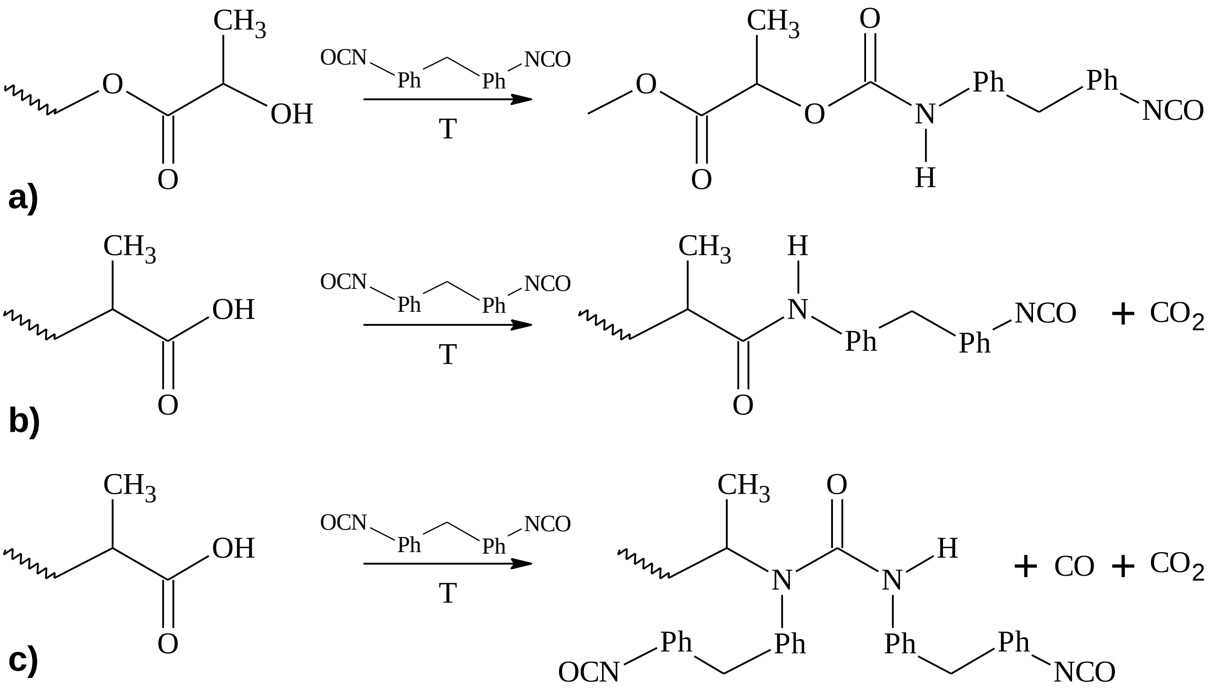
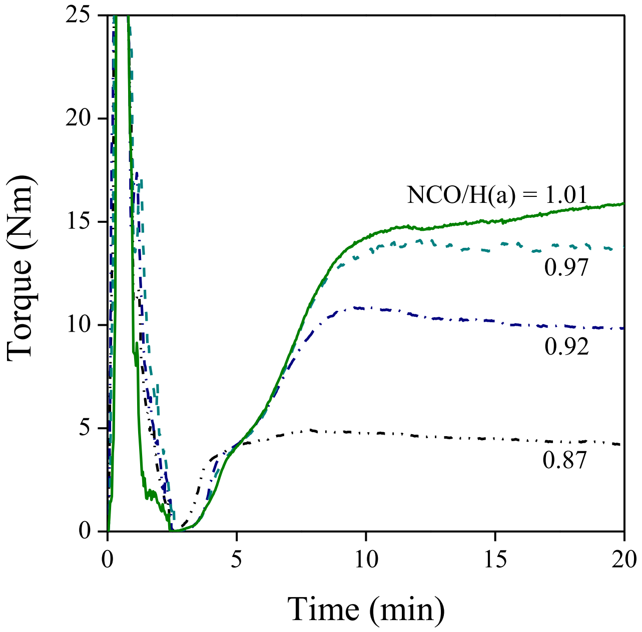
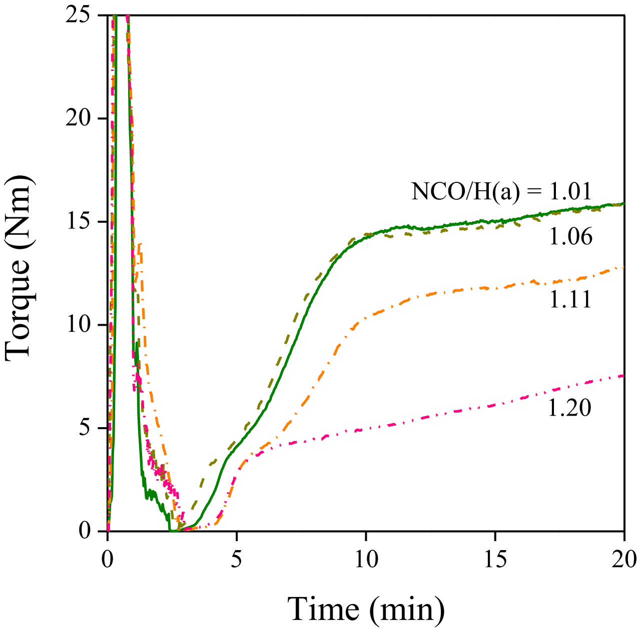


Fig. 1 Hypothetical reactions of MDI with PLA end-groups; a) formation of polyurethane on the hydroxyl end-group, b) formation of amide on the carboxyl end-group, c) formation of acylurea on the carboxyl end-group.



a)



b)

Fig. 2 Changes in torque during reactive blending as a function of time at (a) small and (b) large isocyanate contents with the NCO/H(a) ratio indicated (PLA-b-PU reactive blends containing 0.3 volume fraction PU).

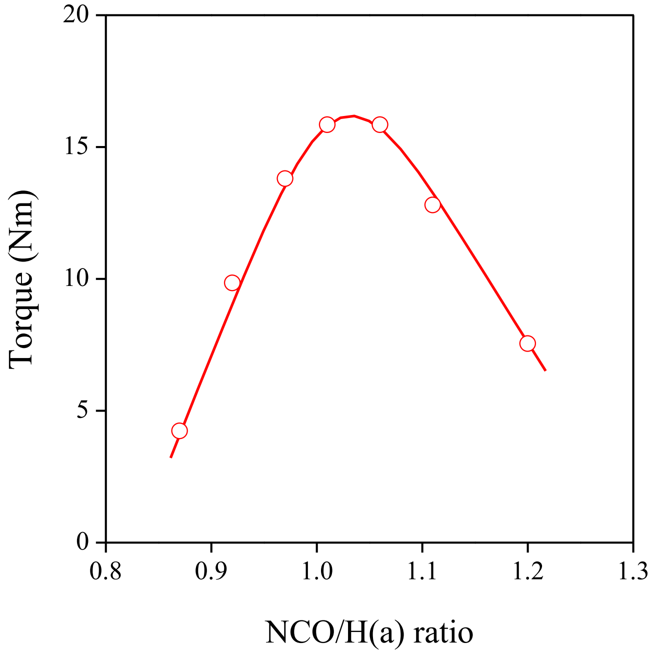


Fig. 3 Torque at the end of the reactive processing as a function of NCO/H(a) ratio.

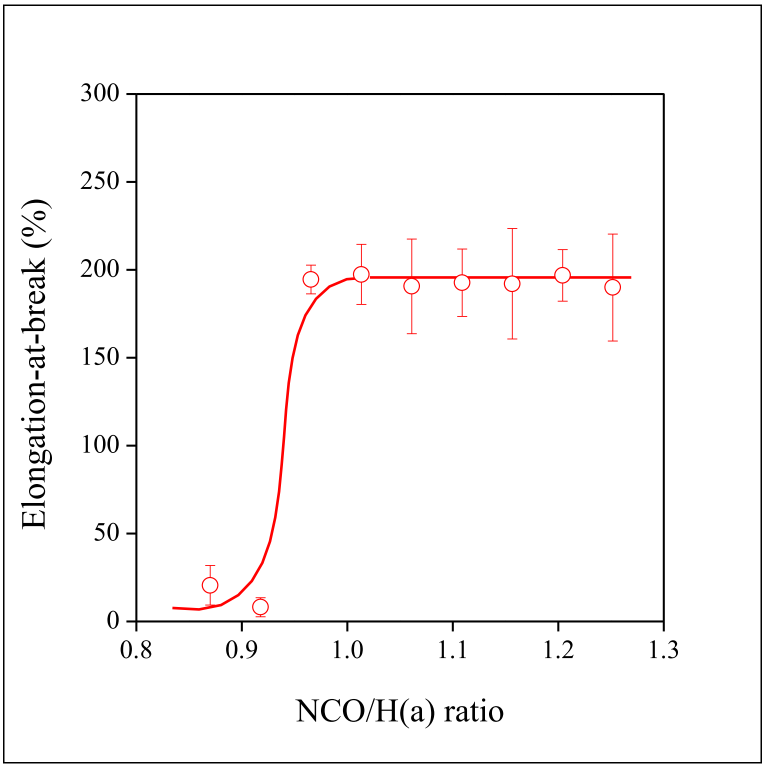
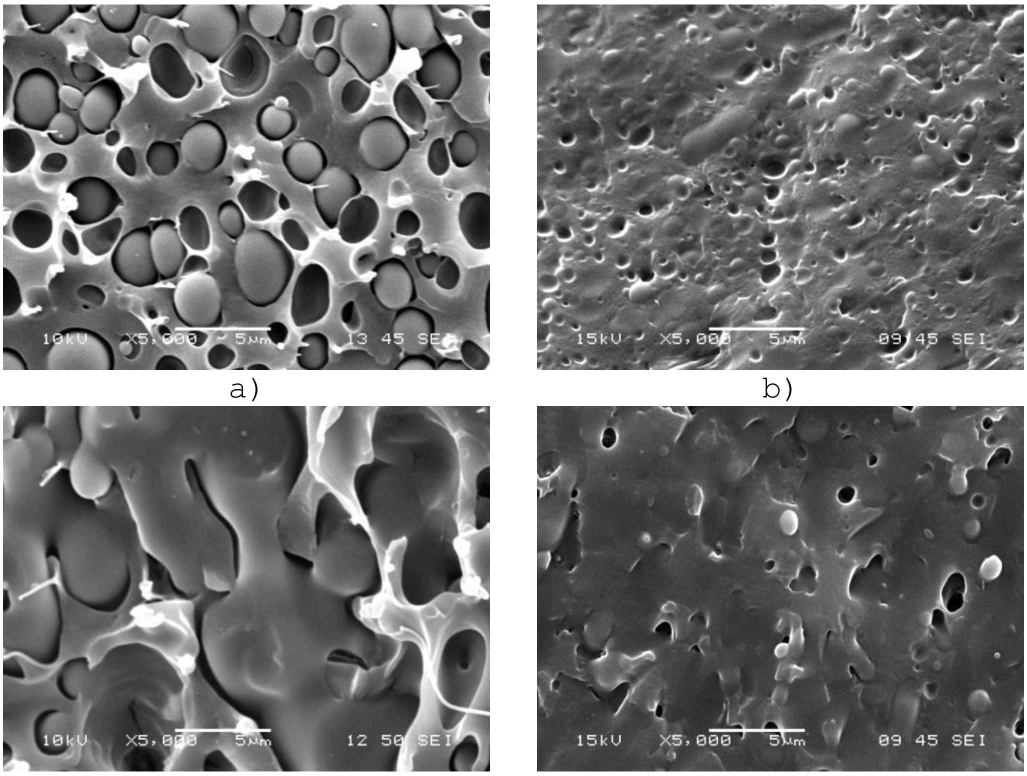
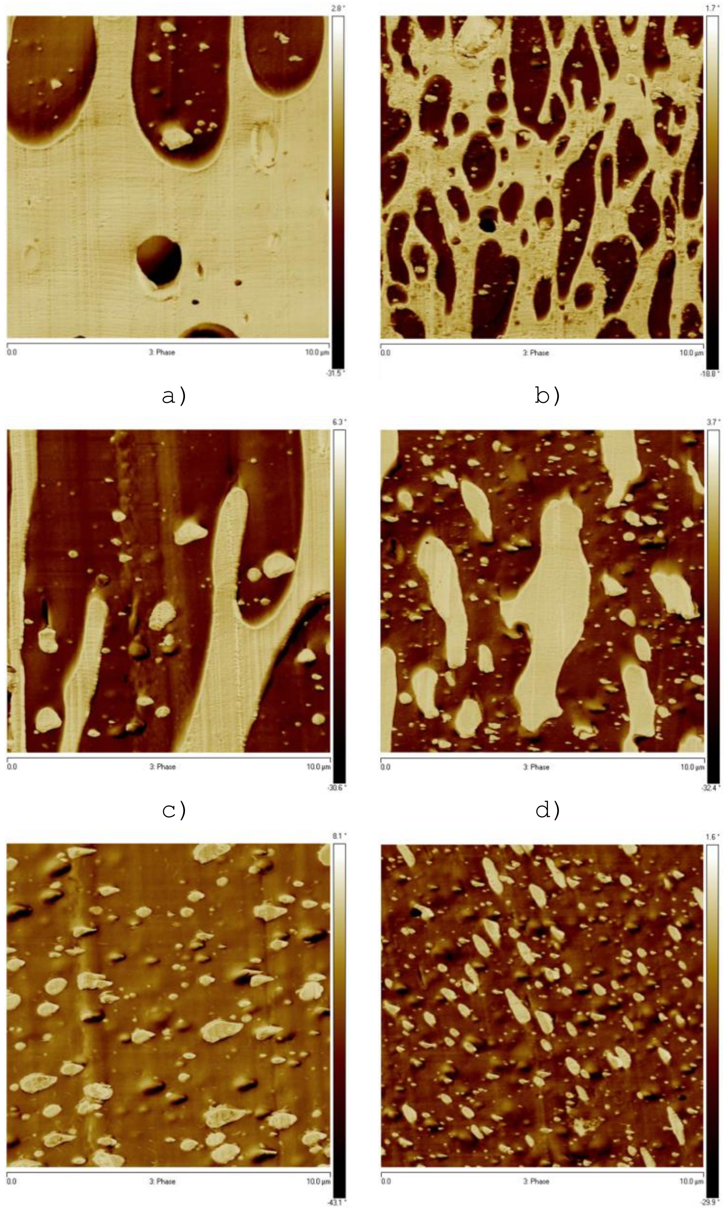


Fig. 4 Elongation-at-break of PLA-b-PU reactive blends plotted as a function of the NCO/H(a) ratio at 0.3 volume fraction polyurethane.



a) b) c) d)

Fig. 5 Morphology of physical (a, c) and reactive (b, d) blends with PLA as matrix containing 0.3 (a, b) and 0.5 volume fraction (c, d) polyurethane elastomer respectively (Magnification: 5000, SEM micrographs taken from cryo-fractured surfaces)



a) b)

c) d)

e) f)

Fig. 6 Morphology of physical (a, c, e) and reactive (b, d, f) blends with PU as matrix containing 0.5 (a, b) 0.3 (c, d) and 0.1 volume fraction (e, f) PLA (tapping mode AFM phase images).

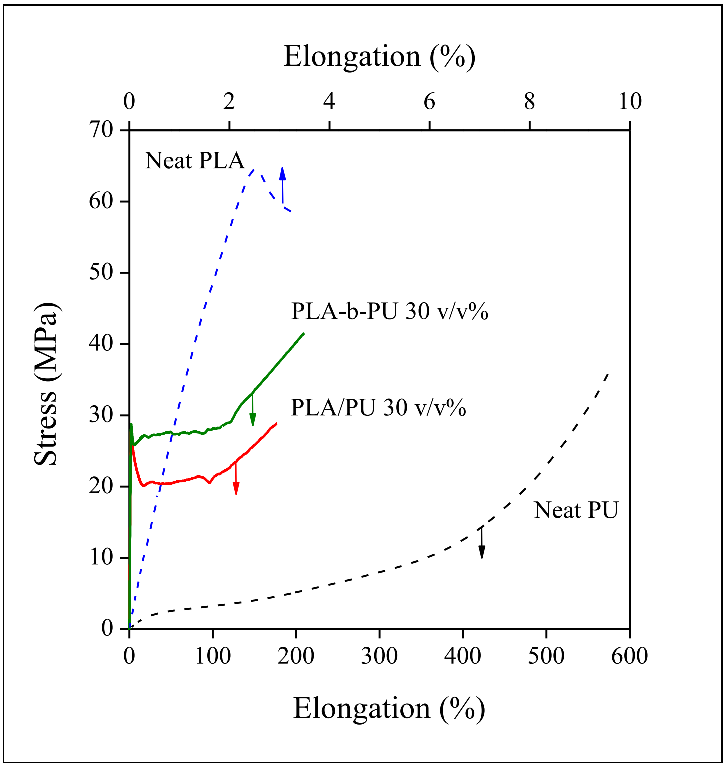


Fig. 7 The effect of composition and processing method on the mechanical behavior of PLA-PU blends.

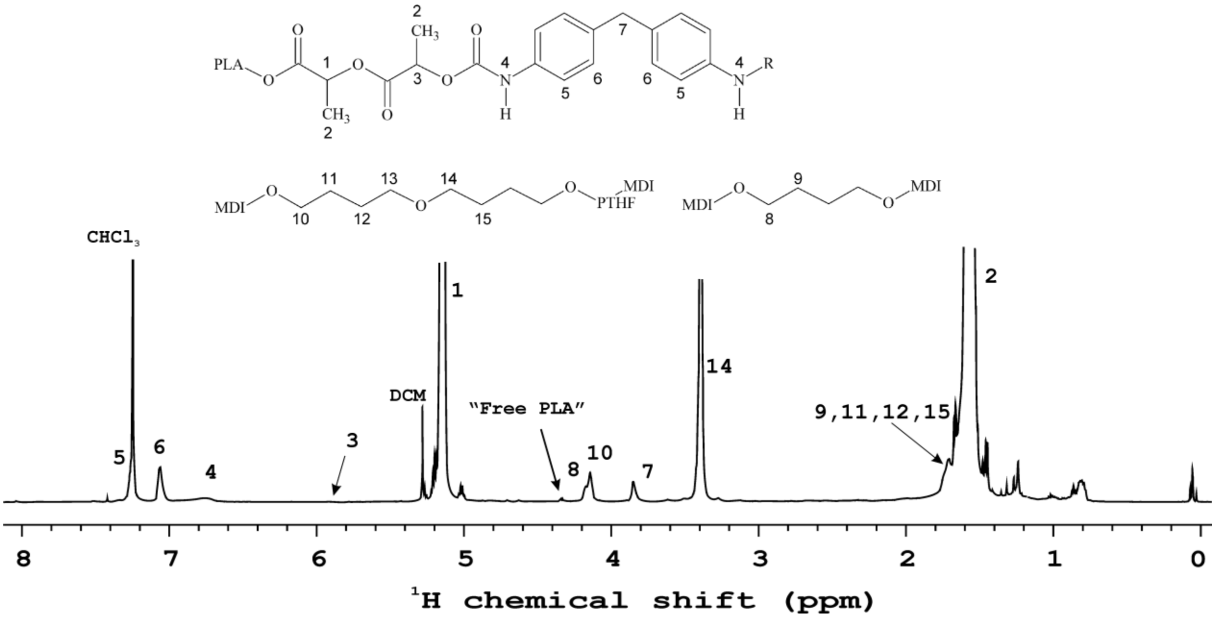


Fig. 8 Solution state ^{1}H NMR spectrum of the reactive blend containing 40 vol% polyurethane recorded in deuterated chloroform at 25 °C. Peaks were assigned using 2D correlation spectra.

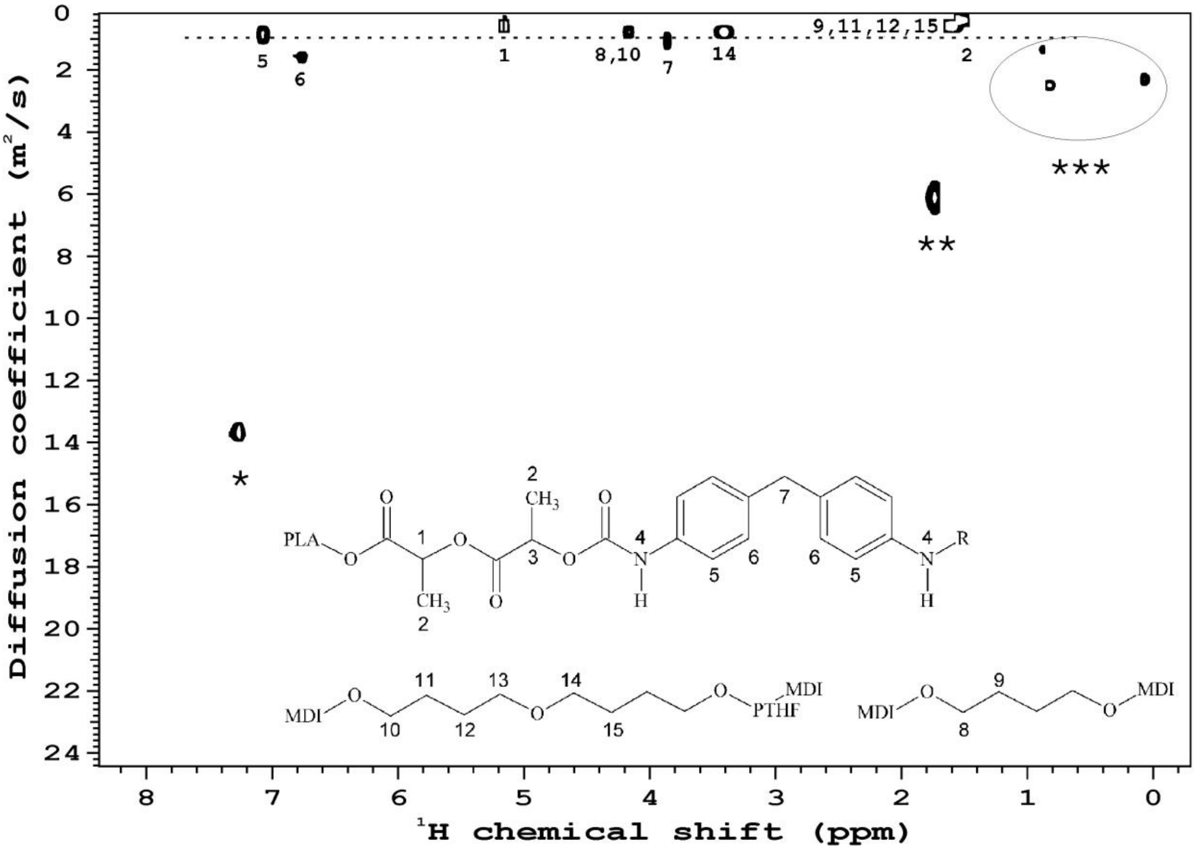


Fig. 9 ^{1}H DOSY spectrum of of the reactive blend containing 40 vol% polyurethane. Signals not belonging to the PLA and PU molecules are denoted with asterisks (*overlapping signal of chloroform with H5; **overlapping signal of water with H9, H11,H12, H15; ***oligomeric impurities).